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PROCESS FOR PRODUCING A THERMAL BARRIER COATING

The invention relates to a process for producing a thermal barrier coating, in which organometal complexes of zirconium and at least one stabilising element selected from the group of the alkaline earth metals or rare earths are provided as starting substances, the starting substances are evaporated by heating and the coating gases which are generated in this way are transported to a component to be coated, which is heated at a deposition temperature, where they are broken down so that a layer is deposited.

Electron beam physical vapour deposition (EB-PVD) processes, in which the substances which are to be deposited on the metallic component, such as for example zirconium oxide, are vaporized in a high-vacuum environment using an electron beam, are known for the production of thermal barrier coatings. On account of the considerable introduction of energy, a thin, molten zone is formed, from which the substances are vapourised and, in a condensation reaction, are deposited on the surface of the component. The layers produced in this way have a columnar structure which tolerates expansion, is better able to withstand alternating temperature stresses and leads to a prolonged service life.

Drawbacks of these processes are the extremely high installation costs for the electron beam gun, for the generation of the high vacuum, for the vacuum chamber and for the partial pressure control. Furthermore, those surfaces of the component which are not directly visible cannot be coated or can only be insufficiently coated during the coating cycle.

EP 0 055 459 A1 has disclosed a process for producing oxide layers by means of chemical vapour deposition (CVD), in which complexes derived from diketones, such as for example

acetylacetonate complexes, are mixed with steam in order to oxidise the metals contained in the complexes and are deposited on a substrate. In the process, the substrate is heated in various applications to temperatures of between 350°C and 800°C. The thicknesses of the deposited layers are in the range between 3.6 and 34 μm. The use of steam as a carrier gas has proven imperative, since oxygen does not enable either reproducibility or deposition to be achieved.

WO 94/21841 has disclosed a flame CVD process for applying inorganic layers to substrates, in which mixed oxides, such as yttrium-stabilised zirconia, are deposited at flame temperatures of from 300°C to 2800°C and pressures which lie well above ambient pressure. The starting substances for the coating gases are passed into the flame and, in a flame CVD process of this type, cannot be heated with a defined temperature cycle and transported to the substrate.

In known processes for producing thermal barrier coatings by means of chemical vapour deposition (CVD), it has hitherto only been possible to produce very thin layers with a low deposition rate and without a columnar structure, which layers also present poor adhesion and, moreover, contain relatively large quantities of undesirable carbon impurities. With a view to industrial use, the selection of the starting substances is of particular importance, since on the one hand they must not be too expensive and on the other hand they must be available in sufficient quantities.

The problem on which the present invention is based consists in providing a process for producing a thermal barrier coating of the generic type described in the introduction in which a thermal barrier coating with good layer properties and a columnar structure is produced as inexpensively as possible.

According to the invention, the solution to this problem is characterized in that the starting substances are heated, at a

process pressure of 0.5 to 50 mbar, to at most 250°C so that the coating gases are formed, and the coating gases are transported to the component to be coated, the surface of which is heated at a deposition temperature of between 300°C and 1100°C.

In this context, it has proven advantageous that thermal barrier coatings which contain zirconium oxide and, for example, yttrium oxide can be produced with a sufficiently great layer thickness of approximately 25 to 1000 μm using the process which is based on the chemical vapour deposition (CVD) principle. Moreover, the thermal barrier coatings produced in this way have a suitable crystal structure and morphology and required layer properties. In terms of their ability to withstand alternating temperature stresses, the layers are comparable to those produced using the EB-PVD process. A further advantage is that, unlike in the electron beam physical vapour deposition (EB-PVD) process, the scattering force of the process means that even those surfaces of the component to be coated which are not directly visible can be coated.

In a preferred configuration, organometal complexes, which are derived from diketones, of zirconium and at least one stabilising element selected from the group consisting of the alkaline earth metals or rare earths are provided as starting substances, since with these components the coating gases are completely broken down or burnt when they come into contact with that surface of the component which has been heated to deposition temperature. Moreover, they have the advantage over alkoxides that they are not sensitive to hydrolysis and are therefore easier to handle.

Furthermore, it is preferable for the coating gases to be mixed with a carrier gas, such as for example oxygen or a mixture of oxygen and argon.

In a further configuration of the process according to the invention, the coating gases or the coating gases and the carrier gas can be transported to the component to be coated, which is arranged in a receptacle, in an admission system which has been heated to at most 250°C.

It has proven expedient for the process to be carried out at a low process pressure of 0.5 to 50 mbar, in order that the coating gases or the coating gases and the carrier gas are transported as quickly as possible, so that their residence time in the hot zone produced by the thermal radiation of the component or substrate which has been heated to the deposition temperature is short as possible and to minimise vapour phase reactions.

Yttrium, lanthanum, calcium, magnesium or cerium are preferably provided as the stabilising element from the group consisting of the alkaline earth metals or rare earths, since they are not excessively expensive with regard to process costs and, furthermore, are available in sufficient quantities for industrial use.

Further configurations of the invention are described in the subclaims.

In the text which follows, the invention is explained in more detail on the basis of exemplary embodiments and with reference to a drawing, in which:

Fig. 1 shows a diagrammatic sectional view through a thermal barrier coating which has been produced using one exemplary embodiment of the process according to the invention, and

Fig. 2 shows a microscopic image of a thermal barrier coating which has been produced using an exemplary embodiment of the process according to the invention, in which image a columnar structure can be recognised.

Fig. 1 shows a thermal barrier coating, which is denoted overall by 1 and has a columnar structure 2, i.e. a fringe crystal structure, which has been deposited on a substrate 4 provided with an adhesion layer 3. In the present exemplary embodiment, the substrate 4 is a surface of a metallic rotor blade of a gas turbine around which hot gases flow in operation. Alternatively, the process can also be used, for example, to coat guide vanes of gas turbines or other parts of internal-combustion engines which are exposed to hot gases.

In the present exemplary embodiment of the process for producing a thermal barrier coating by means of chemical vapour deposition (CVD), first of all an adhesion layer 3 is applied to the surface of the rotor blade 4 around which hot gases flow using a conventional process. The adhesion layer 3 is preferably able to resist corrosion from hot gases and may, for example, be an aluminium diffusion layer, a platinum/aluminium diffusion layer or an MCrAlY cladding layer.

Then, the starting substances for the deposition of the thermal barrier coating 1 by means of chemical vapour deposition (CVD) are provided.

Acetylacetonate complexes of zirconium and yttrium which are in each case in powder form and are mixed in the appropriate ratio to form the desired layer stoichiometry are selected for these materials. Alternatively, the starting substances may also be vapourised separately and mixed in the vapour phase. The starting substances are vapourised or converted into the vapour phase by being heated to at most 250°C, so that the coating gases are formed, and are transported to the rotor blades 4 to be coated. They are transported by means of suitable carrier gases, such as for example oxygen or a mixture of oxygen and argon.

Moreover, those surfaces of the rotor blades 4 which are to be coated are heated, by means of a suitable heat source, at a deposition temperature of between 300°C and 1100°C. This ensures that the coating gases are not heated to over 250°C on their flow path to the rotor blades 4 to be coated. This is effected by, for example, using an admission system which has been heated to at most 250°C and is arranged so as to take account of the heat sources for the components or rotor blades 4, through which system the coating gases and the carrier gas are transported to that surface of the rotor blade 4 which is to be coated.

In the vicinity of those surfaces of the rotor blades 9 which have been heated to the deposition temperature, it may be impossible to completely prevent the coating gases from being heated to this extent on account of thermal radiation. In order to suppress the vapour phase reactions of the coating gases which are possible at elevated temperatures, the thermal barrier coating 1 is produced or deposited at relatively low process pressures of 0.5 to 50 mbar, so that they have a short residence time in the hot zones around the rotor blades 4 which have been heated to deposition temperature. To achieve the low process pressure required for the present vapour phase deposition, the process is carried out in a closed receptacle, to which a pump is connected.

When the coating gases come into contact with those surfaces of the rotor blades 4 which have been heated to deposition temperature, the chemical decomposition of the starting substances occurs and yttria-stabilised zirconia is deposited so as to form the thermal barrier coating 1 and gaseous by-products. Complete decomposition takes place on account of the high deposition temperatures. There are scarcely any carbon impurities. Furthermore, the thermal barrier coating 1 which has been deposited has a columnar structure 2 or fringe crystal structure which is able to tolerate expansion and is of benefit to the resistance to alternating temperature

stresses and to the service life of the thermal barrier coating 1. In the present process, the scatter which is achieved by exploitation of the aerodynamic flow conditions means that not only those surfaces of the rotor blades 4 which are directly visible or exposed to flow, but also all the other surfaces which are exposed to the flow of the coating gases and have been heated, are coated. The by-products are broken down in a downstream pyrolysis furnace and are then filtered and disposed off.

To improve the uniformity of coating, the rotor blades 4 may be moved inside the receptacle. Depending on how the process is controlled, it is possible to deposit thermal barrier coatings 1 with a layer thickness of approximately 25 to 1000 μm on the surfaces of the rotor blades 4, the layer thickness generally lying between 75 and 250 μm. Compared to rotor blades, the thermal barrier coatings 1 deposited on guide vanes of gas turbines often have higher layer thicknesses. To form the thermal barrier coatings 1, deposition in the present uses zirconia partially stabilized with 7-9% by weight of yttria. The process can be used for all parts of a gas turbine or other internal-combustion engines which are exposed to hot gases.